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Electron spectroscopy of carbon materials: experiment and theory

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Abstract. We present a comparative spectroscopic study of carbon as graphite, diamond and C₆₀ using C1s K-edge electron energy-loss spectroscopy (EELS), X-ray emission spectroscopy, and theoretical modelling. The first principles calculations of these spectra are obtained in the local density approximation using a self-consistent Gaussian basis pseudo-potential method. Calculated spectra show excellent agreement with experiment and are able to discriminate not only between various carbon hybridisations but also local variation in environment. Core-hole effects on the calculated spectra are also investigated. For the first time, the EEL spectrum of carbyne is calculated.

1. Introduction

Carbon has the versatility of rehybridization between sp^3 (diamond), sp^2 (graphite) and sp (α -carbyne). It also exists as amorphous carbon and the new nanostructures such as C₆₀ and carbon nanotubes (CNTs) where the hybridisation is intermediate between sp^2 and sp^3 . Two important characterisation tools are X-ray emission spectroscopy (XRS) and electron energy loss spectroscopy (EELS), and it is the purpose of this paper to explore the sensitivity of XRS and EELS to different forms of carbon. In both cases interpretation of spectra is not straightforward, and accurate theoretical modelling is required. This paper explores the ability of density functional calculations to fulfill this role. We obtained a range of carbon spectra and compared with previous calculations, notably performed with plane wave code[1]. After exploring well known spectra we calculate the EEL spectrum of carbyne for the first time.

2. Methodology

2.1. Experiment

2.1.1. X-ray emission: CK α spectra of buckminsterfullerene C₆₀, non-oriented graphite, and diamond nanoparticles were recorded with a laboratory X-ray spectrometer. A sample was located on a copper support, and cooled to liquid nitrogen temperature in the vacuum chamber of the X-ray tube operating with a copper anode (U= 6 kV, I= 0.5 A). Single crystal ammonium

bipthalate NH_4AP was used as an analyzing crystal (this technique for obtaining the $\text{CK}\alpha$ spectrum is described elsewhere[2]). The nonlinear reflection efficiency of the NH_4AP crystal-analyzer allows reliable measurement of $\text{K}\alpha$ emission in the energy region of 275-285 eV. Determination of X-ray band energy is accurate to ~ 0.15 eV with spectral resolution of ~ 0.5 eV.

2.1.2. EELS: Graphite, diamond and C_{60} EEL spectra were acquired using a VG-HB501 Scanning Transmission Electron Microscope, operating at 100kV, equipped with a Gatan EELS spectrometer and an optical CCD camera as a parallel detector. This provides an energy resolution of ~ 0.7 eV. In order to improve the energy resolution, the raw data was treated using the Richardson-Lucy deconvolution method recently developed at Orsay[3]. As a result of this numerical improvement, the energy resolution is around 0.3 eV at the C-K edge.

2.2. Theory

The simulations use AIMPRO, a density functional code[4], under the local density approximation. We apply periodic boundary conditions using a cubic supercell of 54 carbon atoms for diamond with lattice parameter 7.4 Å, 36 carbon atoms for a hexagonal supercell of graphite with lattice parameters 10 Å and 6.56 Å along the basal- and c- axes respectively and a cubic supercell of 60 carbon atoms for a C_{60} molecule with lattice parameter of 13.02 Å, for core and non-core hole calculations. For the carbyne spectrum a tetragonal unit cell of 2 atoms with lattice parameters of 2.62 Å along one direction and 10.58 Å along the other two directions is used. The many body wavefunctions were constructed from a tempered set of 4 radial Gaussians per atom, modified by s and p spherical harmonics (the second smallest Gaussian is augmented by a set of d functions), performing a Bloch sum over lattice vectors. Matrix elements of the kinetic energy and pseudopotentials are found in real space, while Hartree and exchange-correlation energies and potentials are found from a Fourier expansion of the charge density. The Brillouin Zone (BZ) sampling is performed using the generation scheme of Monkhorst and Pack[5]. The k -point separations were 0.01 Å^{-1} , 0.0135 Å^{-1} , 0.0077 Å^{-1} and 0.0382 Å^{-1} for graphite, diamond, C_{60} and carbyne, respectively. The minima in the total energy are obtained using a conjugate gradient algorithm and sampling of $2 \times 2 \times 2$ grid (exceptionally $2 \times 2 \times 20$ for carbyne). The core-EEL and X-ray emission spectra are predicted by calculating p -projected densities of empty and occupied pseudo wavefunctions, respectively. The projected density of states is calculated around a chosen atom by integrating the wavefunctions over a sphere of radius 0.635 Å centered on this atom. The width of the Gaussian function used to broaden each transition was 0.8 eV. The variations in C_{1s} core energy are included as a rigid shift to align σ and σ^* peaks with that of the experimental X-ray and EEL spectra, respectively. The peak heights are then scaled for these same peaks so that the σ and σ^* peak heights match experiment. The core excitation in both spectroscopies generates a core hole which causes the atom with atomic number Z to behave transiently as a $Z+1$ element. Both modelling the excited atom using the $Z+1$ approximation or generating the excited pseudopotentials for carbon gave almost identical spectra for the K-edge of diamond[1]. We use the $Z+1$ approximation, treating the excited carbon atom as a nitrogen impurity. The estimated lifetime of an exciton is $\approx 10^{-15}$ s, and the lattice response time is $\approx 10^{-14}$ s[1]. Thus there is not enough time for the lattice to relax and we therefore use the relaxed ground state structures to obtain our spectra. The calculated EEL spectra of graphite and carbyne are averages of the spectra of inequivalent atoms. However the EEL spectra of diamond and C_{60} are one atom spectra because all atoms are equivalent.

3. Results and Discussion

3.1. X-ray emission

Figure 1 shows our experimental and calculated X-ray emission spectra for (a) graphite, (b) diamond and (c) C_{60} . The calculated spectra with and without core-hole effects are shown

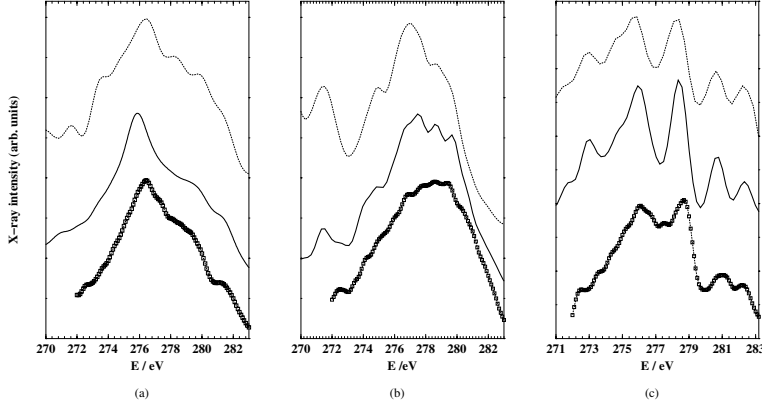


Figure 1. From bottom to top, experimental X-ray emission spectra, first principles X-ray emission spectra without core-hole effects and first principles X-ray emission spectra with core-hole effects, respectively, for (a) graphite, (b) diamond and (c) C_{60} .

as dot-dashed and solid lines, respectively. Overall theory well reproduces the characteristic experimental spectra for diamond, graphite and C_{60} . The three spectra have qualitatively different profiles (graphite has a sharp peak around 277 eV, diamond has a broad bump at the same region and C_{60} has five primary peaks), showing that X-ray emission spectroscopy provides a highly sensitive probe of the bonding state of carbon which is accurately reproduced by theory. We note that the core hole effect need not be applied to X-ray spectra modelling.

3.2. EELS

Figure 2 shows the experimental and calculated EEL spectra for (a) graphite, (b) diamond and (c) C_{60} . As shown in Figure 2, we can distinguish between graphite, diamond and C_{60} spectra. Graphite has a signal dropping to low value for 4 eV after the onset peak (the π^* peak), diamond has a steep onset with no pronounced drop to low signal for at least 14 eV and C_{60} has an onset with individual narrow π^* resonances.

In addition, we have solved the problem of the puzzling (noisy) peak which was obtained between π^* and σ^* in the previous simulated graphite spectrum [1], and also in our calculated spectrum (see top plot of Figure 3). This peak has no equivalent in the experiment. We have studied the spectra of the two different types of carbon atoms in graphite (α and β) and found that their spectra are similar, ruling this out as an explanation of the puzzling peak. However, with applying more k -points these peaks disappear (see bottom plot of Figure 3), showing that the puzzling peaks were due to insufficient number of k -points.

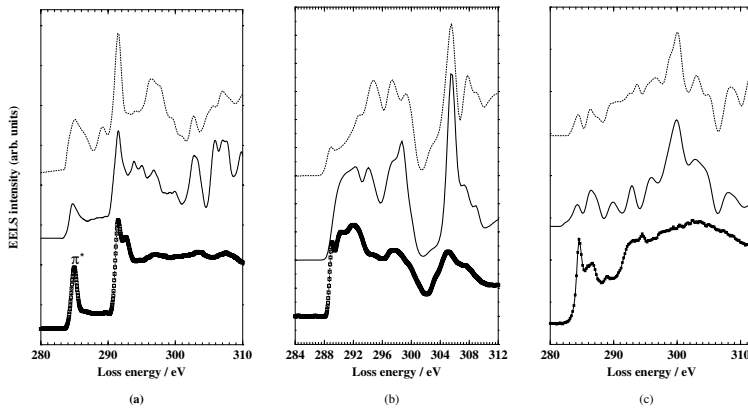


Figure 2. From bottom to top, experimental EEL spectra, first principles EEL spectra without core-hole effects and first principles EEL spectra with core-hole effects, respectively, for (a) graphite, (b) diamond and (c) C_{60} .

We have also studied a carbon with sp hybridization, namely carbyne. Carbyne is a linear carbon, linked by σ - and π - bonds. It has two forms, the polyne $\sim C \equiv C - C \equiv C \sim$ (α -carbyne) and the cumulene $\sim C = C = C = C \sim$ (β -carbyne). Carbyne has semiconductor

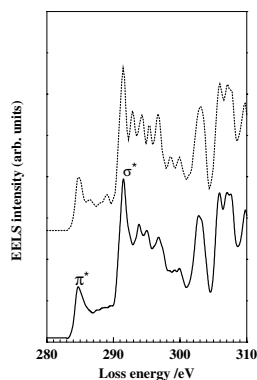


Figure 3. From bottom to top, first principles EEL spectra of graphite using 20x20x20 and 10x10x10 k -point grid, respectively.

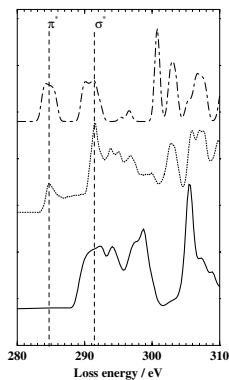


Figure 4. From bottom to top, first principles EEL spectra of diamond, graphite, and α -carbyne, respectively.

properties, high inertness against oxidants and the ability to transform into diamond at high pressures and temperatures[6]. Many experiments have claimed to be succeeded in producing carbynes[7,8]. Also, both the study of low energy loss and Raman spectra of the expanded graphite [9] give another evidence for the existence of carbyne and its distinction from other carbon materials. Therefore, we have studied the EEL spectra of the two different types of carbyne configurations. In Figure 4, we show only the EEL spectrum of α -carbyne which is found to be the closest structure to the experimental spectrum of carbyne[9]. It is clear that the intensity of π^* relative to σ^* in carbyne is sufficiently different (increased) compared with graphite and diamond, that sp hybridization can be identified. Our calculated EEL spectrum of carbyne agrees well with the recent experimental EEL spectrum of carbyne[9].

To conclude, both the calculated X-ray emission and EEL spectra for carbon materials using AIMPRO are in a good agreement with experiment. It is generally known that inclusion of the core-hole effect introduces an energy shift, improving the calculated spectra toward the experiment[1,10]. Because rigid shifts were applied on our calculated spectra, the core hole does not improve either our EEL spectra or X-ray emission modelling. Exceptionally in the EEL spectrum of diamond, the exciton peak (at 289 eV, Figure 2b) is only obtained when the core hole effect is included. This observation agrees with the previous theoretical work[11]. These results show that our method is sufficiently sensitive to local structure to identify sp , sp^2 and sp^3 hybridised carbon, as well as intermediate hybridisation such as shown in C_{60} .

3.3. Acknowledgements

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